

Progress of a novel non-oxide Si-B-C-N ceramic and its matrix composites

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Abstract: In the past twenty years, Si-B-C-N ceramic has attracted wide attention due to its special structure and outstanding properties. The ceramic generally has an amorphous or a nano-crystalline structure, and has excellent structural stability, oxidation resistance, creep resistance and high-temperature mechanical properties, etc. Thus, Si-B-C-N ceramic attracts many researchers and finds potential applications in transportation, aircraft, energy, information, microelectronics and environment, etc. Much work has been carried out on its raw materials, preparation processes, structural evolution, phase equilibrium and high-temperature properties. In recent years, many researchers focus on its new preparation methods, the preparation of dense ceramic sample with large dimensions, ceramic matrix composites reinforced by carbon fiber or SiC whisker, or components with various applications. Research on Si-B-C-N ceramic will develop our insight into the relationship between structures and properties of ceramics, and will be helpful to the development of novel high-performance ceramics. This paper reviews the preparation processes, general microstructures, mechanical, chemical, electrical and optical properties, and potential applications of Si-B-C-N ceramic, as well as its matrix composites.

Key words: Si-B-C-N; ceramic; preparation method; microstructure; property

1 Introduction to Si-B-C-N ceramic

Si-B-C-N ceramic is originally prepared by the organic polymer pyrolyzing route [1,2]. Generally, a kind of special organic polymer precursor, such as solid poly (boro)silazanes or polysilylcarbodiimides, is pyrolyzed at 1000 °C-1400 °C in an inert atmosphere for several hours [3-5]. During the pyrolyzing process, side-chain

groups break; organic molecules with low molecular weight volatilize; crosslinking and curing take place in the polymer precursor. When pyrolyzing is finished, the remaining substance is an inorganic ceramic, mainly consisting of Si, B, C and N. The as-pyrolyzed ceramic generally has an amorphous structure [6], a high structural stability [7,8], a large viscosity and a nice oxidation resistance [9,10]. When the amorphous ceramic is annealed at 1800 °C-2000 °C in an inert atmosphere for several hours, its structure will change into a thermodynamically stable one [8,11]. That is, the amorphous ceramic will crystallize into a nano composite ceramic, with a phase composition of

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B-N-C, SiC and/or Si₃N₄. The as-annealed nano ceramic has high structure stability and nice creep resistance [12,13]. The research of Seyferth *et al* in 1990 shows that the reaction of H₃B·S(CH₃)₂ with (CH₃SiH₂NH)_n cyclic oligomers prepared by the ammonolysis of methylchlorosilane (CH₃SiHCl₂) results in the volatilization of hydrogen and the formation of cross-linked products that contain borazine rings as well as boron atoms, which are linked to three nitrogen atoms [14]. Pyrolysis of the products in an argon stream gives a high yield of black “borosilicon carbonitride”. In 1992, Baldus *et al* employed the aminolysis and polycondensation reactions between tri(chlorosilylamino)borane and methylamine to synthesize poly(boro)silazanes [1]. Pyrolysis of this polymer precursor in an inert atmosphere produces a SiBN₃C ceramic, whose structure is still amorphous even at 1900 °C in the nitrogen atmosphere. In 1996, Riedel *et al* prepared a kind of white poly(boro)silazanes powder, using hydroboration, aminolysis and polycondensation reactions between methylvinylchlorosilane and borane [15]. Pyrolysis of this precursor at 1000 °C in the argon atmosphere produces a kind of Si-B-C-N ceramic, whose structure is amorphous at temperatures lower than 1700 °C in air and does not lose weight even at 2000 °C in an inert atmosphere. At present, using the polymer pyrolyzing route, various kinds of Si-B-C-N ceramics can be prepared, such as bulk ceramic, ceramic fiber, ceramic coating, porous ceramic, ceramic matrix composite or ceramic microdevice [16-19]. These products have found potential applications in aerospace craft, traffic transport system, and micromachine or microcircuit used at elevated temperatures, etc [20].

Besides the organic polymer pyrolyzing route, two other methods are also developed in recent years for the preparation of Si-B-C-N ceramic. In 2005, Vlcek *et al* prepared an amorphous Si-B-C-N film on silicon substrate by a reactive magnetron sputtering technique [21]. The as-deposited film has a smooth surface, high hardness, high structural stability, nice oxidation resistance, controllable electrical resistance and even photoluminescence property [22-24]. In 2007, Yang *et al* developed the mechanical alloying plus sintering method to prepare Si-B-C-N bulk ceramic [25]. They fabricated amorphous Si-B-C-N powder by a high-energy ball mill, using silicon powder, graphite powder and h-BN powder as raw materials. Hot

pressing the as-milled amorphous powder at 1900 °C in the nitrogen atmosphere for 30 min produced a nano composite ceramic, with a phase composition of B-N-C and SiC [26,27].

Because of its special structure and outstanding properties, Si-B-C-N ceramic is widely concerned and studied in the past twenty years or so. Researchers have carried out much work on its raw materials, preparation processes, structural features and high-temperature properties. The number of publications on the topic of “Si-B-C-N ceramic” increases quickly since 1990, as revealed by the statistic data shown in Fig. 1. Currently, important researchers and institutes in the study of Si-B-C-N ceramic, prepared by the organic polymer pyrolyzing route, include Aldinger F, Weinmann M, Bill J, and Seifert H J, *et al* [28-30], in Universitat Stuttgart and Max-Planck-Institut für Metallforschung, Germany; Riedel R *et al* [31], in Technische Universität Darmstadt, Germany; Jansen M *et al* [32], in Universität Bonn, Germany; Sneddon L G *et al* [33], in University of Pennsylvania, USA; Kim D P *et al* [34], in Chungnam National University, South Korea; and Nesper R *et al* [35], in ETH Zurich, Switzerland. Researchers, employing the reactive magnetron sputtering technique to prepare Si-B-C-N film, mainly include Vlcek J *et al* [36], in University of West Bohemia, Czech Republic and Vijayakumar A *et al* [24], in University of Central Florida, USA. In recent years, Jia D C *et al* [37,38], in Harbin Institute of Technology, China, developed the mechanical alloying plus sintering method to prepare Si-B-C-N bulk ceramic. Here, we summarize the current research

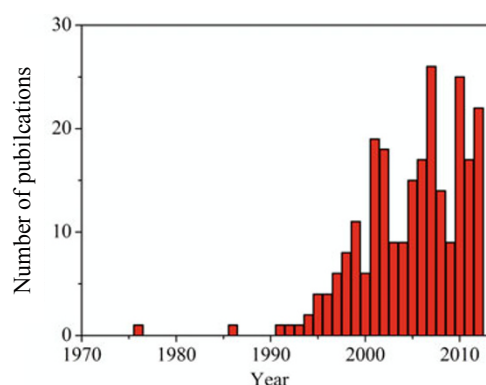


Fig. 1 The number of publications on the topic of “Si-B-C-N ceramic” from 1976 up to 2012. The data come from the statistic of the searching results by <http://scholar.google.com/>.

status of Si-B-C-N ceramic, including its main preparation processes, general microstructures, properties and potential applications, as well as those of its matrix composites.

2 Preparation methods of Si-B-C-N ceramic

So far, organic polymer pyrolyzing route [39], chemical vapor deposit (CVD) [40], reactive magnetron sputtering and mechanical alloying plus sintering technique have been reported to be adopted to prepare different types of Si-B-C-N ceramics [41,42]. The organic polymer pyrolyzing route had been developed and used for more than twenty years. Most of the research results on Si-B-C-N ceramics are obtained by this method and most researchers are still focusing on this method. When the CVD technique is adopted, an organic polymer is deposited on a substrate, and the deposited polymer is then pyrolyzed at high temperatures to produce an inorganic ceramic coating. It has a similar principle like that in the preparation Si-B-C-N bulk ceramic by the organic polymer pyrolyzing route. The reactive magnetron sputtering and mechanical alloying plus sintering techniques are developed in recent years, the results are relatively rare and the studies are still in their infancy.

2.1 Organic polymer pyrolyzing route

For the preparation of Si-B-C-N ceramic by the

organic polymer pyrolyzing route, a kind of special organic polymer, such as poly(boro)silazanes or polysilylcarbodiimides, is required to be synthesized first [43]. When the polymer precursor is heated, side-chain groups will break; organic molecules with low molecular weight will volatilize; dehydrogenation, cross-linking, and polycondensation will occur in the polymer [35]. When temperature is increased to 1000 °C, pyrolyzing finishes and the remaining product is an inorganic ceramic with an amorphous structure [44]. For the preparation of Si-B-C-N ceramic by this method, five steps are generally required: organic polymer synthesis; distillation, cross linking and curing of the polymer; grinding and shaping of the polymer precursor; pyrolyzing of the shaped precursor at high temperatures in an inert atmosphere; and annealing the as-pyrolyzed ceramic at higher temperatures in an inert atmosphere [3,12,39,45-47]. Figure 2 gives a schematic of the preparation process.

(1) Organic polymer synthesis: Monomer organics or oligomers are normally used as raw materials; they are dissolved in organic solvents and then polymerized via hydroboration, amination or dehydrocyclization reactions. Solvents are then volatilized and high polymers are obtained. Take monomer route as an example, the polymer synthetic process generally includes the following steps: First, dissolving methylchlorosilane in toluene, pouring dimethylsulfideborane into the continuously stirred solution slowly at a constant temperature. In this way,

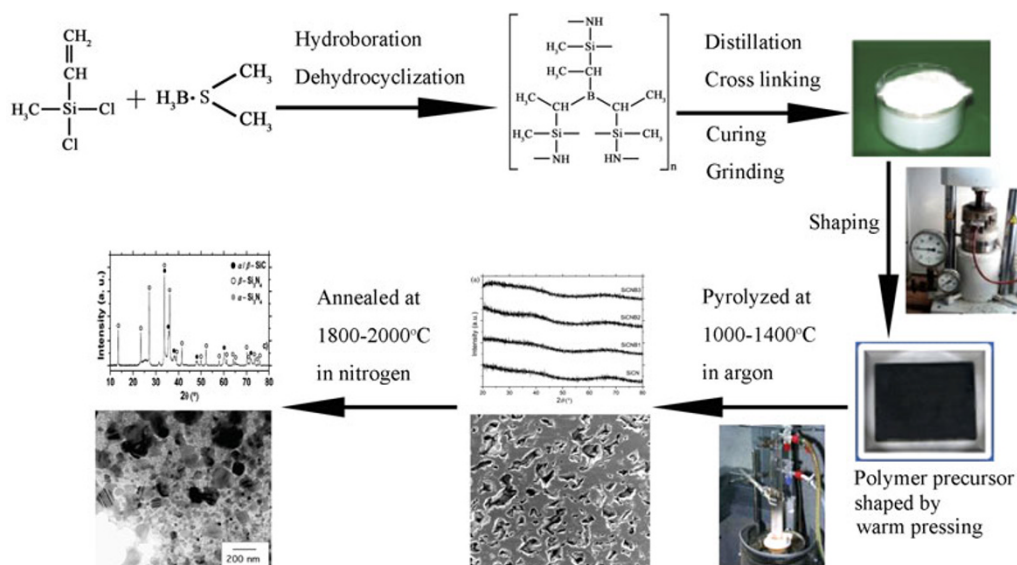


Fig. 2 A schematic showing the preparation process of Si-B-C-N ceramic by the organic polymer pyrolyzing route [12,13,20,29,39,48,49].

hydroboration may occur between the above two organic compounds. Second, stirring the above mixture at room temperature for several hours to volatilize the solvent, and then heating the reaction products in vacuum to remove water and obtain a colorless oily liquid. Third, dissolving the obtained oily liquid in tetrahydrofuran, and continuously stirring the solution in an ammonia stream for several hours. The last, filtering the above mixture and heating the reaction products in vacuum to obtain a solid poly(boro)silazane.

(2) Distillation, cross linking and curing of the synthesized polymer: Heating the obtained solid polymer distiller to 300 °C-400 °C in vacuum and annealing it at this temperature range for several hours. In this way, organic molecules with low molecular weight are removed, and cross linking and curing will occur in the polymer. In the following heating process, the distilled polymer will not melt.

(3) Grinding and shaping of the obtained polymer precursor: The distilled polymer is powdered, and then pressed into a special shape at 200 °C-400 °C in the argon atmosphere.

(4) Pyrolyzing the shaped polymer precursor at high temperatures in an inert atmosphere: Heating the shaped polymer precursor to 1000 °C-1400 °C in the argon atmosphere and pyrolyzing it at this temperature range for 2 h-5 h. An amorphous ceramic containing Si, B, C, and N are prepared.

(5) Annealing the as-pyrolyzed ceramic at higher temperatures in an inert atmosphere: Heating the as-pyrolyzed amorphous ceramic to 1800 °C-2000 °C and annealing it at this temperature range for 3 h-5 h, then the amorphous ceramic will crystallize into a nano composite ceramic.

Due to the difference in raw materials, polymer types, polymer synthetic processes, or polymer pyrolyzing processes, the chemical compositions, microstructures, and properties of the prepared ceramics may be very different. In other words, the structure and the property of the polymer-derived Si-B-C-N ceramic can be tailored by controlling the raw materials or various operation parameters [5]. By this method, various atoms or tetrahedrons are uniformly distributed in the ceramic; the ceramic composition can be adjusted conveniently; the product contains no impurity phase at the grain boundary; and the pyrolyzing process is carried out at relatively low temperatures. However, shortcomings also exist in this

method. For example, raw materials and organic solvents, which are usually very expensive and poisonous, may result in high cost of products, damage to operators and severe pollution to environment. During the polymer pyrolyzing process, a large amount of gas volatilizes, and large mass loss and volume shrinkage occur in the ceramic sample. These may lead to the formation of a large number of pores or even cracks in products [13]. Additionally, the preparation process is complex and the ceramic structure and ceramic property are greatly affected by complicated factors. Generally, the organic polymer pyrolyzing route is applicable to the preparation of ceramic fiber [50], ceramic coating [51], porous ceramic [18], or fiber reinforced ceramic matrix composite [19]. However, by this method, it is difficult to prepare a dense bulk ceramic particularly with large dimensions [12]. Although a pressure assisted pyrolyzing method is developed in recent years and the bulk density of the ceramic is significantly increased [52], the ceramic sample diameter is still around 1 cm or so [12].

2.2 Reactive magnetron sputtering

The reactive magnetron sputtering method is normally used to prepare various films on substrates. In recent years, it is also developed to prepare the Si-B-C-N film on ceramic or metallic substrates [21,53,54]. By this method, a mixture of silicon, graphite and boron are usually used as target, and silicon, silicon oxide or other alloys as substrates. The preparation process mainly includes the following steps. First, the reaction chamber is evacuated and then filled with a mixed gas of nitrogen and argon. Second, the mixed gas is ionized by a glow discharge, and the materials on the target surface are changed into ions or gaseous atoms, because of the bombardment of electrons or nitrogen/argon ions. Finally, atoms from the target and nitrogen ions are deposited on the substrate, forming a ceramic film, containing Si, B, C, and N. The film is usually smooth and amorphous, with a uniform thickness of 1 -5 μm [41]. The diagram in Fig. 3 shows the basic principle of preparing Si-B-C-N film by the ion-beam assisted magnetron sputtering method. The generally used substrates include silicon, silicon oxide, silicon carbide and copper. Silicon plus boron carbide or Si-C-B is usually selected as target [21]. The bias voltage and the temperature of the target are normally set as -100V and 190 °C-450 °C, respectively [23]. The composition, structure and property of the

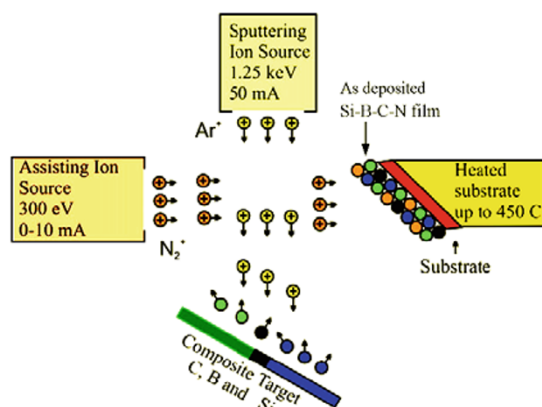


Fig. 3 A schematic showing the principle of preparing Si-B-C-N film by the ion-beam assisted magnetron sputtering system [41].

deposited film can be altered by controlling the composition of the mixed gas or target, the bias voltage or the temperature of the substrate. This method brings little pollution to operator or environment, and can produce ceramic films at relatively low temperatures. It is applicable to the preparation of amorphous Si-B-C-N film on various substrates, but is incompetent to fabricate bulk ceramic or ceramic fiber.

2.3 Mechanical alloying plus sintering method

By this method, silicon powder, graphite powder and h-BN powder are currently used as raw materials, and the preparation process generally consists of two steps, as revealed by the diagram shown in Fig. 4 [26,27,37,55]. First, raw powders, together with silicon nitride or zirconia balls, are put into in silicon nitride

or zirconia jars, and then the jars are sealed under the protection of argon atmosphere. Two jars are fixed on a planetary or vibrating ball mill. After setting milling parameters, the powder mixtures are high-energy ball milled to produce an amorphous Si-B-C-N powder. Second, the amorphous powder is sintered by hot pressing or SPS technique in the nitrogen atmosphere to produce a dense bulk ceramic. For this method, various inexpensive inorganic powders can be used as raw materials, such as powders of silicon, boron, carbon, boron nitride, silicon carbide, silicon nitride, boron carbide, etc; the preparation process is simple and causes little pollution; and more importantly, dense bulk ceramics especially with large dimensions can be easily fabricated. However, using this technology, the distribution of various atoms is not as uniform as that by the organic polymer pyrolyzing route. Densification of the as-milled powder employs a relatively high temperature, which may result in the crystallization of the amorphous powder and is unfavorable for the preparation of dense bulk ceramics with completely amorphous structures. Therefore, the mechanical alloying plus sintering method is applicable to the preparation of dense or porous Si-B-C-N bulk ceramics with simple shapes, but it is inadequate to fabricate ceramic coating, ceramic fiber or ceramic film.

3 Microstructure of Si-B-C-N ceramic

Most of the Si-B-C-N ceramics have a common structural character, that is, no matter the as-pyrolyzed

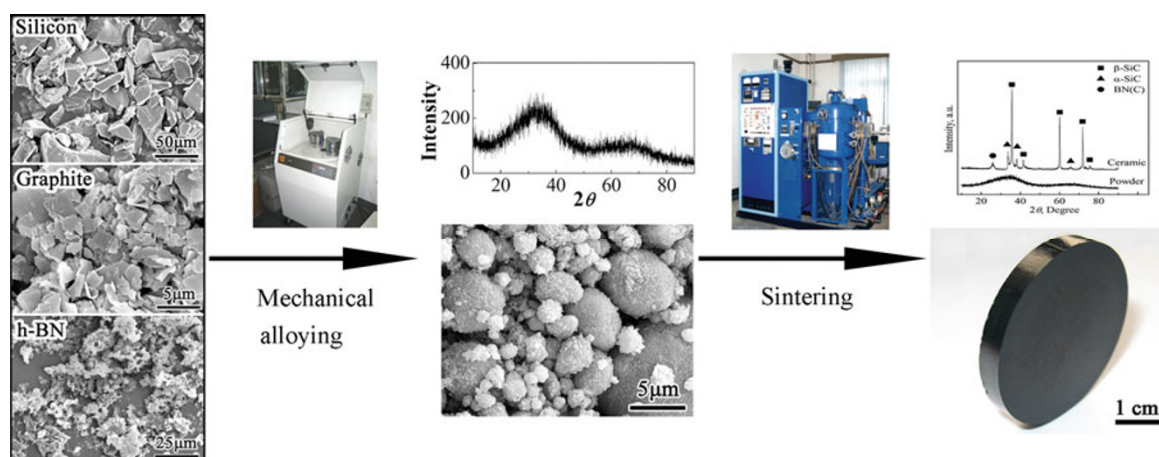


Fig. 4 A schematic showing the preparation process of amorphous Si-B-C-N powder and dense bulk ceramic by the mechanical alloying plus sintering method [26,37,55].

bulk ceramic or ceramic fiber prepared by the organic polymer pyrolyzing route, the as-deposited ceramic film prepared by reactive magnetron sputtering, or the as-milled ceramic powder fabricated by mechanical alloying, they all have amorphous structures [17,41,42]. When they are annealed or sintered at temperatures higher than their preparation temperatures, these amorphous ceramics will crystallize into nano composite ones with the phase compositions of B-N-C, SiC and/or Si_3N_4 [11,37,56]. Generally, the composition homogeneity, structural stability, crystallization process, phase composition and properties of the prepared ceramics are greatly affected by the variation of preparation method, technological process, raw materials or chemical compositions.

3.1 Microstructure of the polymer-derived amorphous Si-B-C-N ceramic

When heating an organic polymer, such as poly(boro)silazane, to 400 °C-600 °C, side-chain groups (Si-CH_3 , NH-Si , C-CH_3) will break, and organic molecules with low molecular weight will volatilize. When the polymer is heated to 1000 °C-1400 °C, most of hydrogen will volatilize, producing an inorganic ceramic with uniformly distributed Si, B, C, and N atoms. Research shows that the as-pyrolyzed ceramic has an amorphous structure, with no identifiable diffraction peaks in its XRD spectrum, as shown in Fig. 5a. The HRTEM image displayed in Fig. 5b reveals that atoms in the amorphous ceramic are thoroughly disordered. The formation of the amorphous structure may be greatly attributed to the uniform distribution of different types of atoms, and to the formation of strong covalent bonds between them.

However, not all the as-pyrolyzed Si-B-C-N ceramics have completely amorphous structures. When raw materials or technical parameters are changed, the as-pyrolyzed ceramic may contain nano crystallites in its amorphous matrix. As indicated in Fig. 6a, the XRD spectrum of this kind of Si-B-C-N ceramic has a weak diffraction peak at about 36° or so, which corresponds to the diffraction of SiC. The peak has a weak intensity and a broad full width at half maximum, suggesting that the crystallites may have a low crystallinity or very small grain size. However, the presence of this diffraction peak suggests that SiC crystallites have formed in the amorphous matrix. The HRTEM image shown in Fig. 6b displays the atomic arrangement in the ceramic. Most areas of the ceramic are composed

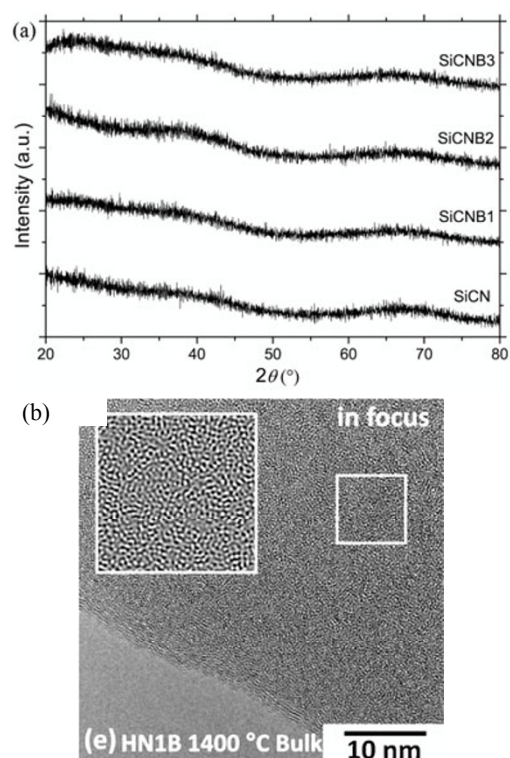


Fig. 5 General XRD spectra (a) [49] and HRTEM image (b) [6] of the as-pyrolyzed Si-B-C-N ceramic.

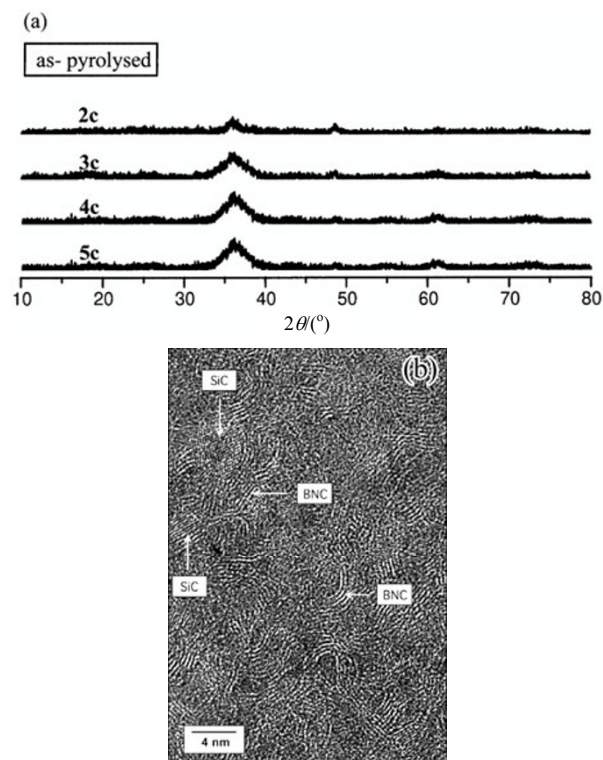


Fig. 6 The XRD spectra (a) and HRTEM micrograph (b) of the as-pyrolyzed Si-B-C-N ceramic, showing the crystallization SiC and B-N-C [7,57].

of disordered atoms, while some zones show the primary conformation of crystallite. The crystallites have very small sizes and mainly consist of SiC and B-N-C, which are different in their interplanar distances and grain shapes. While SiC crystallite has a cubic structure like that in sphalerite, B-N-C more likely possesses a turbostratic structure, similar to that in turbostratic boron nitride. When employing different raw materials, chemical composition, or synthetic processes, the crystallinity of the as-pyrolyzed ceramic may be varied.

The chemical bonding state between different atoms in the amorphous Si-B-C-N ceramic is always not clear, and two conformations are proposed by researchers, as revealed in Fig. 7. In the diagram shown in Fig. 7a, it is thought that the side-chain breaking, gas volatilization, polymer cross linking and polycondensation may produce an inorganic ceramic with a rather uniform distribution of Si, B, C and N atoms. Because of the formation of strong covalent bonds between different atoms, the atomic diffusion and the crystallization may be very difficult. These are

considered important factors contributing to the formation of amorphous structure and to the high structural stability of the as-pyrolyzed ceramic. This model is most likely an inference from the molecular structure and the pyrolyzing process of organic polymers. However, many research results provide evidences for the other model [32], as shown in Fig. 7b. By this model, it is considered that the as-pyrolyzed Si-B-C-N ceramic consists of two kinds of amorphous phases: amorphous $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) and turbostratic B-N-C. They have rather small sizes and very uniform distribution in the ceramic. At the boundary between the two phases, chemical bonds, such as, Si-C-B, Si-C-N, and Si-N-B, may exist. It is generally considered that B-N-C is not only hard to crystallize, but also can block atomic diffusion and suppress grain growth of SiC. As a result, it greatly contributes to the formation of amorphous structure and the structural stability of the as-pyrolyzed ceramic.

3.2 Structural stability of the polymer-derived amorphous Si-B-C-N ceramic

It is found that the polymer-derived amorphous Si-B-C-N ceramic has a rather high structural stability. The ceramic has little weight loss even at 2000 °C in an inert atmosphere, as suggested in Fig. 8a. The weight stability is better than that of Si_3N_4 or Si-C-N ceramic, which shows severe weight loss at temperatures higher than 1500 °C in the same atmosphere. The higher structural stability of the Si-B-C-N ceramic may be related to its special structure described in Fig. 7b. The uniformly distributed B-N-C retards atomic diffusion and lowers the activity of carbon atoms. Additionally, it wraps $\text{SiC}_x\text{N}_{4-x}$, resulting in the blocking of gas release, the increasing of local nitrogen pressure, and the suppression of decomposition or crystallization. It is also found that when the amorphous ceramic is heated in an inert atmosphere, it does not crystallize even at 1700 °C, as revealed in Fig. 8b. Because of the formation of strong covalent bonds, the small size and the uniform distribution of each phase, the atomic diffusion may be very difficult, thus crystallization is prohibited. When the as-pyrolyzed amorphous ceramic is heated to a temperature between 1800 °C-2000 °C, it will crystallize into nano composite ceramic, consisting of B-N-C, SiC and Si_3N_4 . When the temperature is higher than 2000 °C, Si_3N_4 will decompose and the nano ceramic is composed of

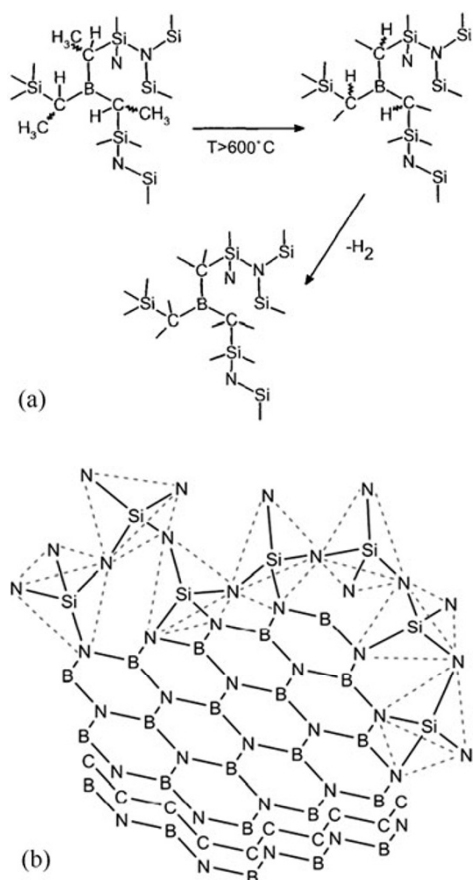


Fig. 7 Two structural schematics of the polymer-derived amorphous Si-B-C-N ceramics [29,46].

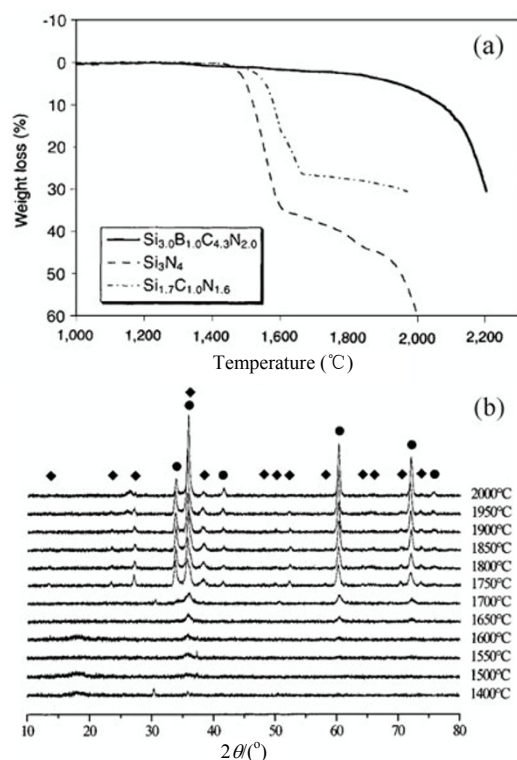


Fig. 8 The thermogravimetric curve of the polymer-derived amorphous Si-B-C-N ceramic in the helium atmosphere (a) [15], and the XRD patterns of the Si-B-C-N ceramics annealed at different temperatures for 3 h in the nitrogen atmosphere (●, α -SiC; ◆, β -Si₃N₄) (b) [8].

B-N-C and SiC. When raw materials or polymer synthetic process changes, the crystallization or decomposition temperature of the as-pyrolyzed ceramic may be varied.

Results from thermodynamic calculation show that the polymer-derived amorphous Si-B-C-N ceramic actually has a metastable structure. The images shown in Fig. 9 are three isothermal sections of the calculated

Si-B-C-N phase diagram, with a boron content of 15 at.% and a nitrogen pressure of 1 bar. For example, when the chemical composition of the ceramic is located in the phase region of Si₃N₄+SiC+C+BN at 1400 °C, the stable ceramic should consist of these four kinds of crystals, as suggested in Fig. 9a. When the temperature is increased to 1600 °C, Si₃N₄ will react with free carbon to form Si and N₂, and the stable ceramic will be composed of Gas+SiC+C+BN, as indicated in Fig. 9b. Of course, if higher content of nitrogen or silicon is contained, the stable ceramic may consist of Gas+Si₃N₄+SiC+BN or Liquid+Si₃N₄+SiC+BN at 1600 °C. At 2000 °C, the residual Si₃N₄ may decompose, and the stable ceramic will be made up of Gas+SiC+C+BN or Gas+Liquid+SiC+BN. The above discussion reveals that the stable Si-B-C-N ceramic at a standard atmosphere is actually a composite ceramic, consisting of crystals of simple substances or compounds. The amorphous structure is metastable, and its formation may be due to the changed thermodynamic or kinetic conditions in ceramic. When the amorphous ceramic is used at high temperatures for a long duration, it may crystallize, decompose or lose weight, and macro deformation may occur to the ceramic components.

3.3 Structure and its stability of the as-annealed nano Si-B-C-N ceramic

Annealed at 1800 °C-2000 °C for several hours, the as-pyrolyzed amorphous Si-B-C-N ceramics may crystallize and most of them may change into nano composite ceramics with phase compositions of SiC, Si₃N₄ and B-N-C. The results in Fig. 10 reveal the typical XRD spectra and HRTEM image of the as-annealed nano Si-B-C-N composite ceramic. The

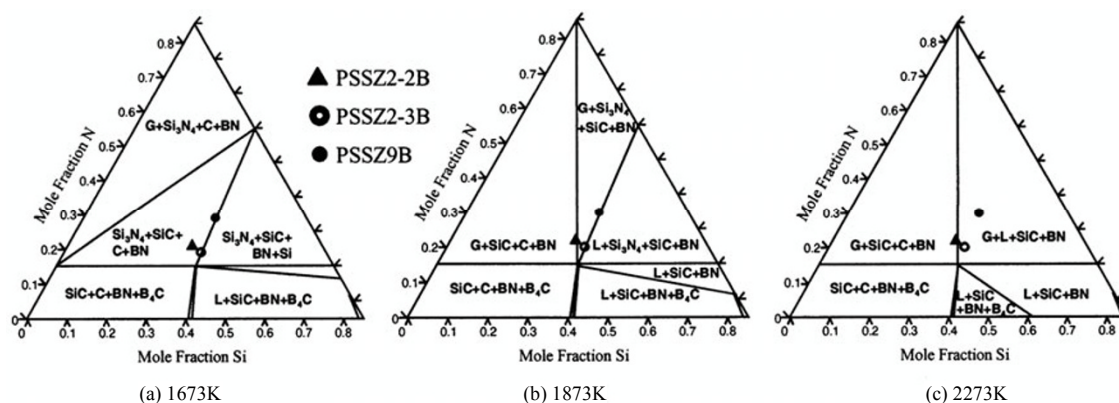


Fig. 9 Isothermal sections of the calculated Si-B-C-N phase diagram with 15 at.% boron and 1 bar N₂ at three different temperatures [58].

grain sizes of SiC and Si₃N₄ are around 100 nm, and most of the grains contain a large amount of stacking faults, twins, or disordered atoms, etc, as shown in Figs. 10b and 11a. Additionally, areas with disordered atoms also exist next to the crystal grains. The appearance of Si₃N₄ at such high temperatures may be attributed to the special structures of the ceramic. B-N-C wraps Si₃N₄ grains, retards the reaction between Si₃N₄ and carbon, increases the nitrogen pressure, and hence depresses the decomposition of Si₃N₄. Being different from SiC and Si₃N₄, B-N-C has no fixed shape and a much lower crystallinity. The results in HRTEM image suggests that B-N-C has a turbostratic structure, similar to that in turbostratic boron nitride, as shown in Fig. 11b. It is generally considered that B-N-C is composed of alternately arranged atomic layers of turbostratic carbon and turbostratic boron nitride. This phase is not only hard to crystallize, but greatly affects the structural stability and the crystallization process of Si-B-C-N ceramic.

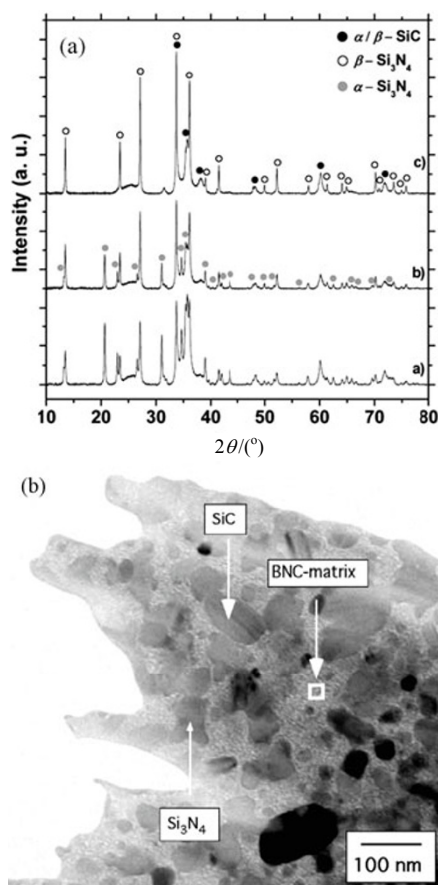


Fig. 10 XRD patterns (a) [29] and bright field image under TEM (b) [48] of the as-annealed Si-B-C-N ceramics.

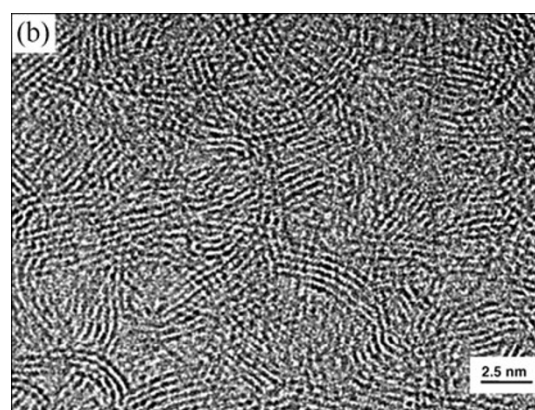
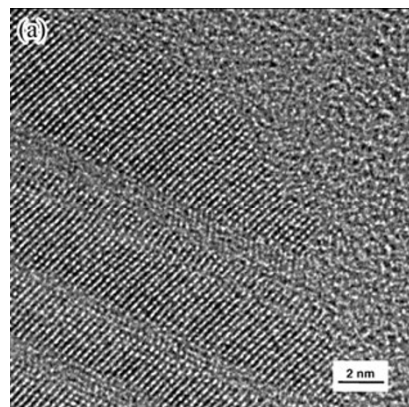


Fig. 11 The HRTEM image of the Si-B-C-N ceramic annealed at 1800 °C/Ar/5h (a), and that of the B-N-C phase in the ceramic annealed at 2000 °C/Ar/5h (b) [11].

The phase composition of the as-annealed nano Si-B-C-N ceramic may be varied, if raw materials or polymer synthetic process changes. One important case is that the as-annealed nano ceramic only consists of SiC and B-N-C, no Si₃N₄. The results shown in Fig. 12 reveal the microstructure of this kind of nano Si-B-C-N ceramic. SiC has a grain size of about 100 nm, and B-N-C has no fixed shape, lower crystallinity and a turbostratic structure. The phases are uniformly distributed in the ceramic. Research shows that this kind of ceramic may start to crystallize at a temperature lower than 1600 °C [30], lower than that of the nano ceramic consisting of SiC, Si₃N₄ and B-N-C. However, thermogravimetric analysis reveals that this kind of Si-B-C-N ceramic has little weight loss even at 2100 °C [30], indicating a higher resistance to decomposition.

3.4 Structure and its stability of the Si-B-C-N film prepared by reactive magnetron sputtering

The Si-B-C-N film, prepared by the reactive

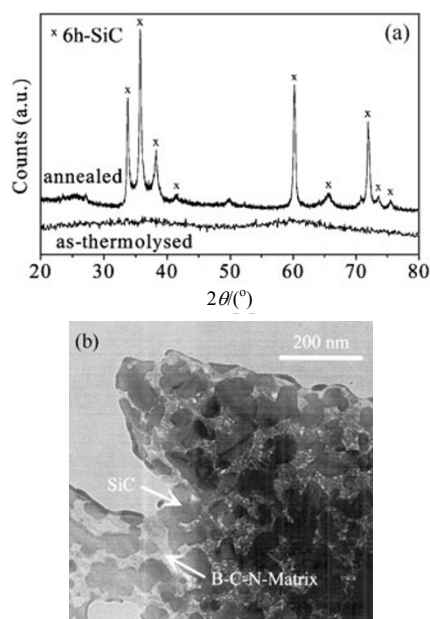


Fig. 12 The XRD spectrum (a) and bright field image under TEM (b) of the crystalline Si-B-C-N ceramic annealed at 1800 °C/N₂/3h, showing another kind of phase composition [59].

magnetron sputtering technique, generally has a smooth surface, a thickness of 1-5 μm, an amorphous structure and a good structural stability, as revealed by the results presented in Fig. 13. It is found that the as-deposited Si-B-C-N film has a completely amorphous structure with high stability. The XRD spectra of the films have no identifiable diffraction peaks, coinciding with the results from HRTEM images. When annealing the film at 1600 °C in the argon atmosphere, it may not crystallize and still keep the amorphous structure, suggesting a high structural stability. The thermogravimetric analysis shows that the film may not lose weight at 1600 °C in an inert atmosphere, as suggested by the curve shown in Fig. 13b. At higher temperatures, sharp and severe decomposition and weight loss occur. It is evident that the as-deposited Si-B-C-N film has a lower decomposition temperature than that of the organic polymer derived bulk Si-B-C-N ceramic. This may be related to the homogeneity and the bonding states of various kinds of atoms, and further research is required in this subject. Additionally, the crystallized Si-B-C-N film mainly consists of Si₃N₄, somewhat different from that of the polymer-derived nano Si-B-C-N ceramic.

3.5 Structure of the Si-B-C-N ceramic prepared by mechanical alloying plus sintering

To prepare Si-B-C-N ceramic by the mechanical

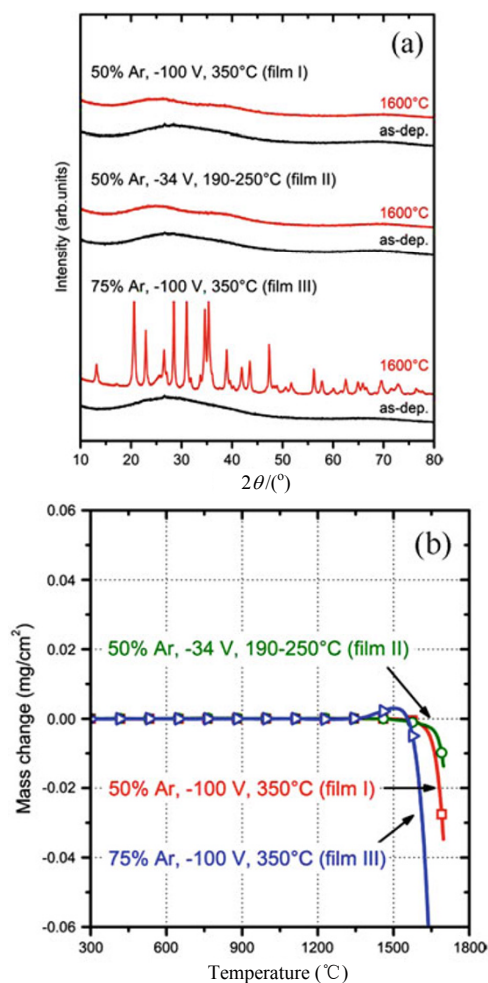
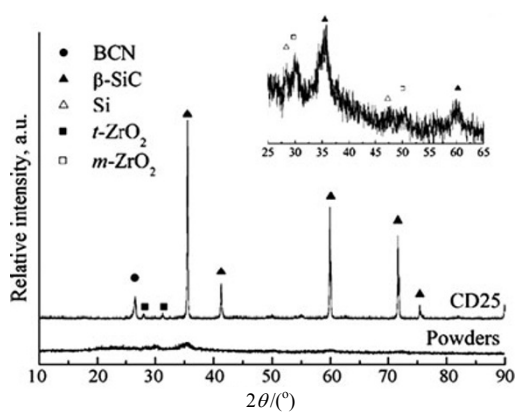
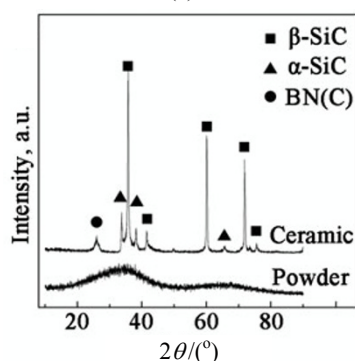


Fig. 13 XRD spectra of the as-deposited Si-B-C-N films and the films annealed at 1600 °C in argon (a), and thermogravimetric curves of Si-B-C-N films in helium up to 1700 °C (b) [56].

alloying plus sintering method, amorphous Si-B-C-N powder should be prepared by high-energy ball milling first, and the as-milled amorphous powder is then sintered at a high temperature under certain pressure to fabricate dense bulk ceramic. At present, the usually used ball mills include vibrating ball mill and planet ball mill. While the former produces a powder with crystallites or impurity [60], the latter normally generates a well amorphous Si-B-C-N powder [42]. From the XRD results displayed in Fig. 14, it is found that the powder prepared by vibrating ball mill generally has an amorphous structure, although containing weak diffraction peaks of SiC and zirconia. SiC crystallites come into being during the high energy ball milling process, and zirconia comes from the wear of zirconia balls or jars. In contrast, the powder, prepared by a planet ball mill with silicon nitride balls and jars, has no identifiable diffraction peaks,



(a)



(b)

Fig. 14 The XRD spectra of the mechanically alloyed Si-B-C-N powders and sintered ceramics prepared by a vibrating ball mill with zirconia balls and jars (a) [60] or a planet ball mill with silicon nitride balls and jars (b) [37].

indicating a nice amorphous structure.

Sintered at high temperatures for 30 min in the nitrogen atmosphere, the XRD spectra of the prepared ceramics suggest that the amorphous structures have crystallized and the as-sintered bulk ceramics normally consist of SiC and B-N-C, as revealed in Fig. 14. From the bright field images under TEM shown in Fig. 15, it is found that while the sintered ceramic with zirconia impurity has a SiC grain size of 200-500 nm, the ceramic prepared using the nice amorphous powder free from impurity just has a SiC grain size of about 100 nm. Additionally, as compared to that in the former ceramic, B-N-C in the latter ceramic has a small size, a lower crystallinity and a more uniform distribution. It is inferred from the above results that the zirconia impurity may enhance atomic diffusion, favor crystallization and promote grain growth. The distribution and crystallinity variation of B-N-C may greatly contribute to the difference in ceramic microstructures.

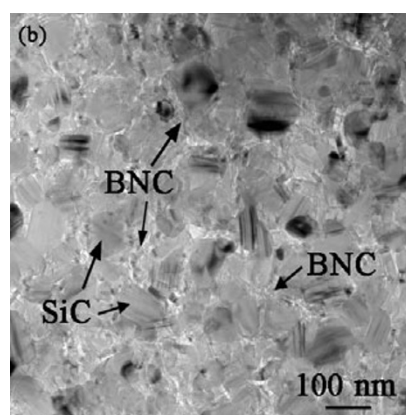
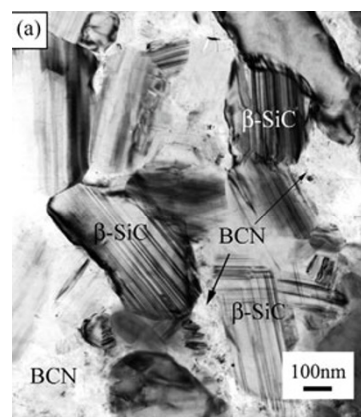


Fig. 15 The bright field images under TEM of the ceramics prepared using the impurity-containing (a) [26] and impurity-free (b) Si-B-C-N powder [27].

4 Properties of Si-B-C-N ceramic

4.1 Mechanical properties of Si-B-C-N ceramic

4.1.1 Creep resistance of the polymer-derived Si-B-C-N bulk ceramic

During the organic polymer pyrolyzing process, a large amount of gas will volatilize from the sample, because of the decomposition of the polymer precursor. As a result, large volume shrinkage and large weight loss will occur in the sample, resulting in the appearance of a large number of pores or even cracks in products. Thus, the preparation of dense bulk ceramics particularly with large dimensions and the evaluation of mechanical properties are difficult. Up to now, the mechanical property research of the polymer-derived bulk Si-B-C-N ceramic is limited to the creep resistance at elevated temperatures [13,61,62].

Figure 16 shows the creep curves of the polymer-derived amorphous and nanocrystalline Si-B-C-N ceramics. It is found that when the amorphous ceramic is hold at 1400 °C under a pressure

of 5 MPa for 30 h, the sample shows a deformation of about 1%. At the same time, the deformation rate drops quickly. In the next 240 h, the deformation rate always keeps a small value, and the total deformation of the sample is about 0.5%. In contrast, although the nanocrystalline ceramic is hold at 1500 °C under 5 MPa for 270 h, the total deformation of the sample is smaller than 0.1%. It is believed that the different microstructures in these two kinds of ceramics lead to the variation of their creep behaviors. The amorphous ceramic has a metastable structure, which will crystallize and change into nano ceramic at high temperatures under a certain pressure. The crystallization process will be accompanied by various phenomena, such as nucleation, atomic diffusion, grain boundary sliding, and grain growth etc. These phenomena will lead to the change of ceramic microstructure and the macroscopic deformation of ceramic sample. When most of the amorphous structures turn into crystals, turbostratic B-N-C will retard the long-range diffusion of atoms, hinder the grain boundary sliding and depress the grain growth. As a result, the creep rate of the ceramic sample is greatly lowered and it becomes more difficult for further deformation.

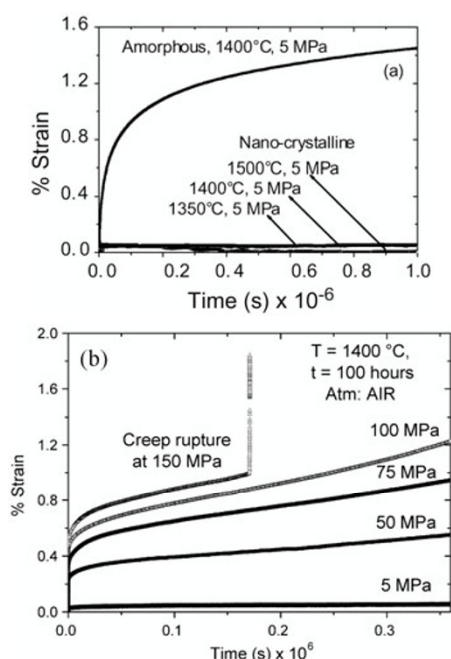


Fig. 16 Strain curves of amorphous and nano-crystalline Si-B-C-N ceramics as a function of time. (a) Strain curves of amorphous and nano-crystalline Si-B-C-N ceramics under a constant pressure of 5 MPa [62]; (b) Strain curves of the nano-crystalline Si-B-C-N ceramic under various loads at 1400 °C in air [13].

In contrast, nanocrystalline Si-B-C-N ceramic has a more stable structure, since it has been annealed at high temperatures for hours. The as-annealed ceramic consists of uniformly distributed nano grains, and no intergranular phase with low melting point exists in the grain boundary. Thus, the nanocrystalline ceramic has a better creep resistance and the ceramic sample exhibits a small deformation. Figure 16b shows the creep curves of nanocrystalline Si-B-C-N ceramics. When the ceramic sample is hold at 1400 °C under a pressure of 50 MPa for 100 h, the total macroscopic deformation is smaller than 0.6%, indicating an excellent creep resistance.

4.1.2 Property of the polymer-derived Si-B-C-N fiber

Because of its high structural stability and nice oxidation resistance, Si-B-C-N fiber is expected to be a kind of high-performance ceramic fiber with potential applications in high temperature environments. Table 1 provides the mechanical, thermal and physical properties of Si-B-C-N fiber, SiC fiber and the user's requirements. Si-B-C-N fiber can be used at 1500 °C in air, which is superior to SiC fiber. In the argon atmosphere, Si-B-C-N fiber has a tensile strength of about 2.3 GPa at 1500 °C, and its elastic modulus at 1400 °C is 80%-90% of the value at room temperature. After exposure to air at 1500 °C for 50 h, the tensile strength of the Si-B-C-N fiber is about 80% of the value at room temperature, but the retained strength of SiC fiber approaches to zero. The Si-B-C-N fiber also has a breaking elongation of about 0.7%-1.5%, a good flexibility, a small density, a low thermal expansion coefficient and a nice resistance to melt silicon. These advantages make Si-B-C-N fiber the only kind of ceramic fiber that satisfies the requirements of users, who may adopt the fiber to fabricate ceramic or resin matrix composites applied at elevated temperatures.

4.1.3 Mechanical property of the Si-B-C-N film prepared by reactive magnetron sputtering

Vlček *et al* [23] prepared Si-B-C-N films on silicon or silicon oxide using the reactive magnetron sputtering method, and then evaluated their mechanical properties. As revealed in Fig. 17, employing the optimized technical parameters, the as-deposited film may have a Vickers hardness, an elastic modulus, and an elastic recovery of about 44 GPa, 240 GPa, and 82 %, respectively. Among various factors, the bias voltage and the temperature of substrate have stronger influence on these mechanical properties. The compressive stress between the film and the substrate

Table 1 Performance comparison between Si-B-C-N fiber and several typical SiC fibers, as well as the requirements of potential users [17,63-65]

Properties	Requirements of the European Turbine Manufacturers	SiBN(C) Bayer Uni Bonn	SiC Dow Corning	SiC (Hi-Nicalon) Nippon Carbon	SiCTiO (Thyranno Lox E) Ube Industries
Oxygen content (% in weight)	-	1.0	0.2	0.8	0.3
Microstructure	-	Amorphous	Crystalline	Partial Crystalline	Crystalline
Max. temperature usable in air, °C	1500-2000	1500	1300	1200	1000
Tensile strength					
at room temperature (RT), GPa	3.0	3-4	3-4	3	ca. 3.2
at 1400 °C in Ar (% of RT-value)	-	95	95	70	95
at 1500 °C in Ar, GPa	2.5	2.3	-	-	-
Strength after exposure to air (% of RT-value)					
at 1300 °C for 100 h	-	-	-	23	55
at 1500 °C for 50 h	-	80	-	0	-
E-modulus					
at RT, GPa	300	200-350	420	300	200
at 1400 °C in Ar (% of RT-value)	83	80-90	-	70	-
Breaking elongation, %	1.0	0.7-1.5	0.6	1.0	1.5
Creep parameter*	>0.4	0.8	0.4	0.1	0.7
Subcritical crack growth	-	No	Yes	No	Yes
Coefficient of thermal expansion, $\times 10^{-6}/K$	3-5	3.5	4	3.3	4.5
Thermal conductivity, W/(m·K)	-	>3	46	5	64
Resistance to molten silicon	-	Yes	No	No	No
Density, g/cm ³	<5	2	3.1	2.74	2.5
Diameter, μm	10-150	8-14	10	14	12
Flexibility	Good	Good	Medium	Good	Good

*: Bend-stress-relaxation measurements at 1400 °C

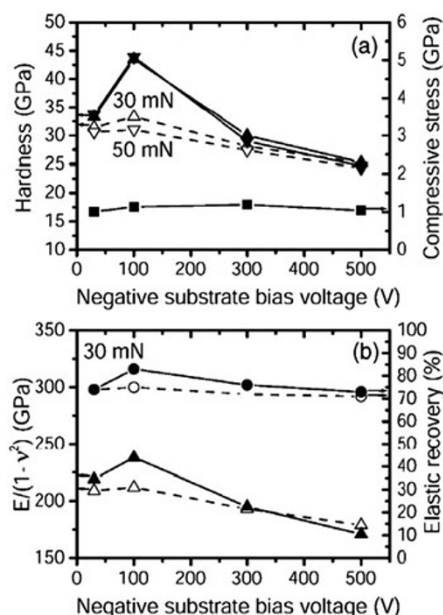


Fig. 17 Mechanical properties of the Si-B-C-N films prepared using a C-S-B (20:60:20%) target at various negative substrate bias voltages in a 50% N₂+50% Ar gas mixture for $T_s=350$ °C (full symbols) and $T_s=180-250$ °C (empty symbols) [23].

is about 1 GPa, which is slightly affected by the variation of preparation conditions. A small compressive stress indicates a nice lattice match at the interface, and the film is not easy to flake.

4.1.4 Mechanical property of the Si-B-C-N ceramic prepared by mechanical alloying plus sintering

By the mechanical alloying plus sintering method, it is easy to prepare dense bulk ceramic particularly with large dimensions, and various mechanical properties can be conveniently evaluated. This is superior to the organic polymer pyrolysing route. The ceramic sample prepared by this method generally has a diameter of 30-50 mm, with a bulk density of 2.5-2.8 g/cm³. The bulk density approaches to that of the polymer-derived bulk Si-C-N ceramics or the magnetron sputtered Si-B-C-N films. Table 2 lists the room-temperature and high-temperature mechanical properties of the ceramics hot pressed at 1800 °C, 1850 °C or 1900 °C under a pressure of 40 MPa or 80 MPa in the nitrogen or argon atmosphere for 30 min. Using the powder prepared by a single-step-milling route [27,66], the CS1900 ceramic sintered at 1900 °C has

Table 2 Mechanical properties of the bulk Si-B-C-N ceramics, hot pressed at 1850 °C or 1900 °C under a pressure of 40 MPa in the nitrogen atmosphere for 30 min [26,27,67].

Ceramic sample	Flexural strength (MPa)			Young's Modulus (GPa)	Fracture toughness (MPa·m ^{1/2})	Vickers hardness (GPa)
	RT	1000 °C	1400 °C			
CS1850	191.7±20.7	-	-	107.9±9.5	1.80±0.07	2.44±0.31
CS1900	312.8±5.2	287.2±15.5	225.3±15.1	136.3±17.8	3.31±0.02	4.17±0.50
CD1900	423.4±43.0	375.4±10.7	260.4±15.7	134.6±13.5	3.09±0.05	3.89±0.43
CA1800	421.9±27.3	-	-	174.1±10.2	3.40±0.15	12.74±0.32
CN1800	526.8±10.4	-	-	222.1±27.7	5.25±0.20	11.63±0.49
1900°C/80MPa	331.1±40.5	-	-	139.4±16.0	2.7±0.4	4.7 ± 0.2

room-temperature flexural strength, Young's modulus, fracture toughness and Vickers hardness of about 312.8 MPa, 136.3 GPa, 3.31 MPa·m^{1/2}, and 4.17 GPa, respectively. The flexural strength and Young's modulus are approximately one-third of those of the hot-pressed SiC ceramics, and the fracture toughness is slightly lower than that of the latter. At 1000 °C and 1400 °C in air, the ceramic sample still has a flexural strength of about 287.2 MPa and 225.3 MPa, respectively. When hot pressing the powder prepared by a two-step-milling route at 1900 °C under 40 MPa for 30 min [27], the obtained CD1900 ceramic possesses a room-temperature flexural strength and Young's modulus of about 423.4 MPa and 134.6 GPa, respectively. The relatively higher flexural strength and lower Young's modulus indicates a favourable resistance to thermal shock. When aluminum was added in raw powders, the CA1800 or CN1800 ceramic hot pressed at 1800°C has a flexural strength of about 400-550 MPa. However, the Si-B-C-N ceramic free from any impurity or additive and hot pressed at 1900 °C/80 MPa just has a flexural strength of about 331.1 MPa. Obviously, the mechanically alloyed Si-B-C-N powder is hard to densify, and the introduction of zirconia or aluminum may promote its sintering and hence improve the room temperature mechanical properties of the hot pressed Si-B-C-N ceramic.

4.2 Oxidation resistance of the Si-B-C-N ceramic

4.2.1 Oxidation resistance of the polymer-derived Si-B-C-N ceramic

The results from thermogravimetric analysis indicate that the polymer-derived Si-B-C-N ceramic has an oxidation resistance even better than SiC or Si₃N₄ ceramic, as revealed by the results shown in Fig. 18a. When heating ceramic fragments in an air flow, the oxidation of SiC and Si₃N₄ occurs at about 1050 °C and 1200 °C, respectively. However, Si-B-C-N ceramic

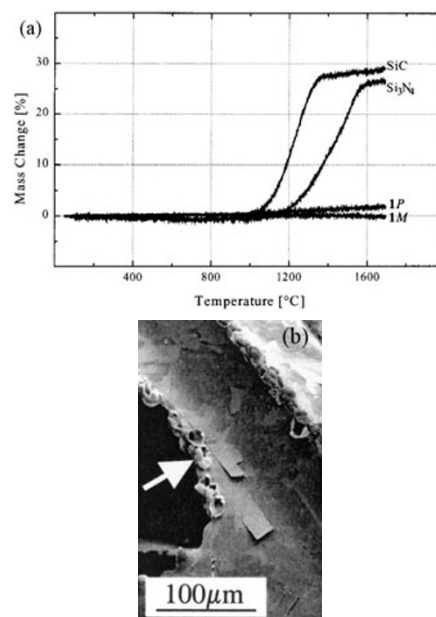


Fig. 18 Thermogravimetric curves of Si-B-C-N ceramic powders tested in air [10] (a), and surface morphology of the Si-B-C-N bulk ceramic oxidized at 1500 °C in air for 24 h (b) [67].

has little weight change even at 1700 °C. It is inferred that the excellent oxidation resistance of this kind of ceramic may be due to the complex structure of the oxidation film formed on the ceramic surface during heating process, and this has been partially confirmed by the experimental results on Si-B-C-N bulk ceramic and ceramic fiber. The image shown in Fig. 18b is the surface morphology of the ceramic oxidized at 1500 °C for 24 h. It is found that bubbles only appear at the edges of the ceramic particle, while on the flat surface, the oxidation film is uniform and unbroken. The results from Raman analysis reveal that the oxidation products in the edges mainly contain cristobalite and that in the flat surface still have an amorphous structure. The inclusion of boron atoms in the oxidation film may retard its crystallization.

The image in Fig. 19a displays the cross section of a Si-B-C-N fiber oxidized at 1500 °C in air for 2 h. The oxidation film on this fiber is uniform and compact, with a thickness of about 2 μm . Under TEM, the oxidation film is found to have a quite dense multilayer structure, as suggested by the image shown in Fig. 19b. The outer layers have a large content of silicon oxide, and are easy to crystallize. The inner layers are mainly composed of amorphous Si-B-C-N-O and various kinds of boron nitride. Boron nitride is rich in inner layers and lack in outer layers. At high temperatures in air, boron and nitrogen atoms in the surface layer of the ceramic may form boron nitride. While boron nitride in inner layers is hard to be oxidized, that in outer layers is easy to be oxidized and the oxidation products are easy to volatilize. On the other hand, the non-volatilized boron oxide may dissolve in silicon

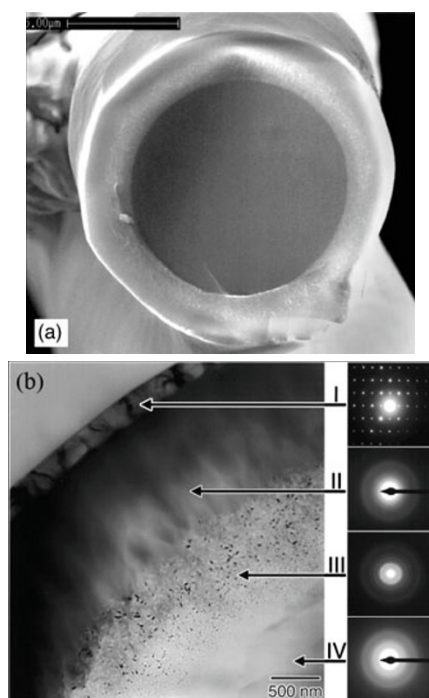


Fig. 19 Cross section of the Si-B-C-N ceramic fiber oxidized at 1500 °C in air for 2 h (a), and TEM image of a cross section (along fiber axis) of the oxidized portion of a fiber heated at 1500 °C for 2 h in air, indicating four distinct zones with their corresponding electron diffraction patterns: (I) surface layer of α -cristobalite with diffraction pattern ([100] zone axis); (II) homogeneous layer of amorphous silica; (III) mixed layer of SiBCNO glass with BN precipitates, diffraction pattern shows hexagonal BN reflections with strong contribution of (0002) planes; (IV) core of fiber, which remained unchanged (b) [68].

oxide and form a complex structure in the oxide film. This film may have a proper viscosity and perfectly cover the ceramic surface, retarding the diffusion of oxide atoms and preventing the further oxidation of the ceramic.

4.2.2 Oxidation resistance of the Si-B-C-N film prepared by reactive magnetron sputtering

The Si-B-C-N film prepared by the reactive magnetron sputtering technique also possesses a good oxidation resistance, as revealed by the thermogravimetric curve displayed in Fig. 20. It is found that the Si-B-C-N film sputtered with the B_4C -Si target shows extremely high (up to 1400 °C) and very high (up to 1600 °C) oxidation resistance. However, the oxidation of the SiC substrate starts at temperatures above 1100 °C. Further research indicates that the mass change of the film after oxidation in air up to 1700 °C is caused by the formation of oxide layer on the film surface [69]. The oxide layer is amorphous, has a thickness of about 1 μm , and mainly consists of almost stoichiometric SiO_2 , with a small content of boron, nitrogen and carbon. It is inferred that the inclusion of boron in the surface layer may greatly contribute to the maintenance of the amorphous state of the oxide layer, and this is similar to that of the oxidation layer on poly-derived Si-B-C-N bulk ceramic or ceramic fiber.

4.2.3 Oxidation resistance of the Si-B-C-N ceramic prepared by mechanical alloying plus sintering

The oxidation of the bulk Si-B-C-N ceramic, prepared by the mechanical alloying plus sintering method, is also evaluated by the thermogravimetric analysis in an air flow with a heating rate of 10 °C/min, as shown in

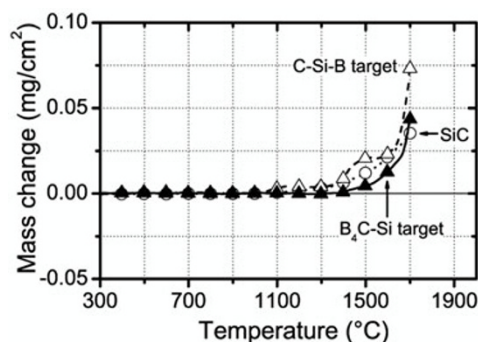


Fig. 20 Thermogravimetric analysis of as-deposited Si-B-C-N films in a pure air at a heating rate of 10 °C/min. The films were prepared using a C-Si-B (5:75:20%) or B_4C -Si (25:75%) target in a 50% N_2 +50% Ar gas mixture. For comparison, the data obtained for the SiC substrate are also presented [69].

Fig. 21. The ceramic sample CS2H1900 shows little mass change up to 1500 °C, indicating a great oxidation resistance in such conditions. After oxidized at 1200 °C in dry air for 5 h or 85 h, the oxidation layer on the ceramic surface is coarse, and has lots of cracks on its surface [70]. The layer has a thickness of about 5-10 μm, and mainly contains crystalline SiO₂, with a small content of nitrogen and carbon, and little content of boron. These are very different from that of the oxidation layers on polymer-derived or as-deposited Si-B-C-N ceramics. Probably, the crystallization and the little boron content in the oxidation layer are attributed to the crystallized structure of the as-sintered ceramic and the inhomogeneity of various atoms. Further research is required on the relationship between the microstructure and the oxidation resistance of the as-sintered Si-B-C-N bulk ceramic. Additionally, recent research shows that the addition of AlN or ZrO₂ in raw powders may reduce the oxidation resistance of the hot pressed Si-B-C-N ceramic at the temperature range of about 1000-1400°C, and these results will be further studied and published in another article.

4.3 Electrical and optical properties of Si-B-C-N ceramic

4.3.1 Electrical property of the polymer-derived Si-B-C-N ceramic

The electrical conductivity of the polymer-derived Si-B-C-N ceramic may dramatically change before and after being annealed at high temperatures, as indicated in Fig. 22. By pyrolyzing poly(boro)silazane at 1000 °C in the argon atmosphere for hours, the prepared amorphous Si-B-C-N ceramic has a

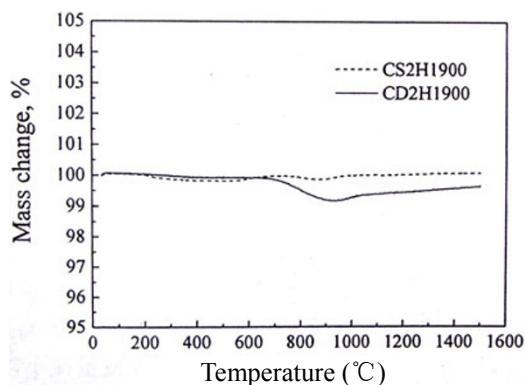


Fig. 21 Thermogravimetric curve of CS2H1900 and CD2H1900 ceramics in an air flow with a heating rate of 10 °C/min [70].

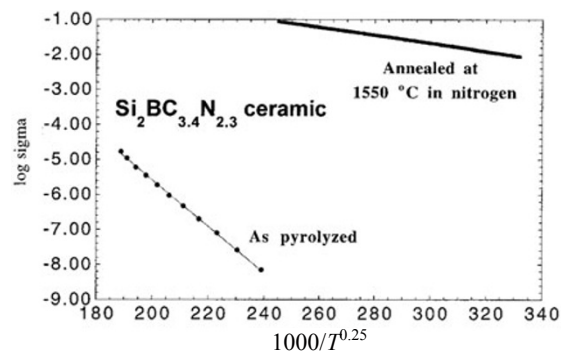


Fig. 22 Conductivities of as-pyrolyzed and as-annealed Si-B-C-N ceramics as functions of temperature [71].

conductivity of about $10^{-8} \Omega^{-1}\cdot\text{cm}^{-1}$. This value is about four orders larger than that of as-pyrolyzed Si-C-N ceramic, and this may be related to the doping of boron atoms or the formation of crystallites in the ceramic. When annealed the amorphous Si-B-C-N ceramic at 1550 °C in the nitrogen atmosphere for 12 h, its conductivity is quickly increased to about $10^{-1} \Omega^{-1}\cdot\text{cm}^{-1}$. The rapid conductivity increase may be attributed to the loss of nitrogen during the annealing process [71]. The variation of the conductivity with the change of temperature before and after annealing fits the VRH model, indicating that the ceramics all have amorphous structures, and the as-annealed ceramic may contain a large amount of unsaturated bonds. Because of the excellent structural stability and the electric conductivity at high temperatures, polymer-derived Si-B-C-N ceramic may be widely used in microelectronic circuits applied at elevated temperatures, such as filament, conductive coating or semiconductor device based on PN junction.

4.3.2 Electrical and optical properties of the Si-B-C-N film prepared by reactive magnetron sputtering

The results presented in Fig. 23 reveal the influence of the nitrogen content in the air flow on the electric resistivity and the photonic gap of the as-deposited Si-B-C-N film. When the air flow contains no nitrogen, the electrical resistivity of the film is about $0.209 \Omega\cdot\text{m}$. With the increase of the nitrogen content, the electrical resistivity of the deposited film shows a rapid rise. When the nitrogen content is 20%, the electrical resistivity is dramatically enhanced to $1.4 \times 10^6 \Omega\cdot\text{m}$. It is also found that when the nitrogen content is higher than 30%, the electrical resistivity may be much larger

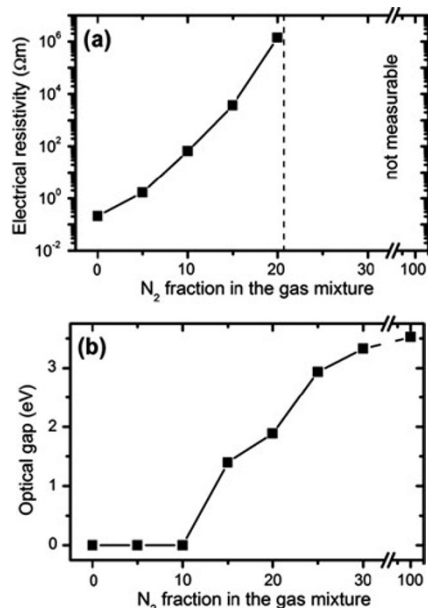


Fig. 23 Influence of the nitrogen content in airflow on the electrical resistivity (a) and the optical gap (b) of Si-B-C-N ceramic film [72].

than $10^8 \Omega\cdot\text{m}$ [72]. These results suggest that the as-deposited Si-B-C-N film with small nitrogen content may be a semiconductor, while a large amount of nitrogen is included, the film may turn into an insulator. Research shows that the optical gap of the as-deposited Si-B-C-N film also greatly relies on the nitrogen content in the air flow, as shown in Fig. 23b. When the nitrogen content is smaller than 10%, the optical gap of the prepared film is nearly zero. When nitrogen content is higher than 10%, the optical gap of the film starts to increase, and the value reaches to 2-3 eV when the nitrogen content is between 20%-30%. Results from theoretical calculation suggest that the electrical and optical property variation of the as-deposited film may be related to the doping of nitrogen atoms, which may split the valence bond of atoms. Additionally, the Si-B-C-N film also exhibits other physical or thermal properties, such as photoluminescence, small thermal conductivity and thermal expansion coefficient [24].

5 Potential applications of Si-B-C-N ceramics

5.1 Applications of the polymer-derived Si-B-C-N ceramic

Since polymer precursors have a proper viscosity when they are heated, various common shaping technics can be employed here, such as casting, injection molding, pressure forming, tape casting, drawing, dipping, painting and impregnation, as indicated in Fig. 24. By shaping and then pyrolyzing the organic polymer precursor, many kinds of products can be prepared, including bulk ceramic, ceramic fiber, porous ceramic, ceramic coating, ceramic matrix composite, and components with various shapes. Because of the especially high structural stability, nice oxidation resistance, high creep resistance, and other outstanding properties, these products can be used to fabricate high-performance materials or components applied at elevated temperatures, such as the nose cone in high-speed aircraft, the brake block in high-speed vehicle, the filter or absorber in water or gas purification installation, and the micro-sized components in microdevice, micromotor or microcircuit [20]. Thus, the polymer-derived Si-B-C-N ceramic may be widely used in transportation, aircraft, energy, information, microelectronics, environment, etc.

Currently, most of the products prepared by the polymer pyrolyzing route are bulk ceramics or ceramic fibers. The bulk ceramic has a diameter of about 1 cm, as shown in Fig. 25a. Since polymer pyrolyzing will produce a large amount of gas, and large weight loss and volume shrinkage will occur in the precursor, the preparation of ceramic sample especially with large dimensions is difficult. Although a pressure-assisted pyrolyzing method is developed in recent years [52], the size of the bulk ceramic is still not increased considerably. Micro component with a dimension of hundreds of microns can also be fabricated by this method, as displayed in Fig. 25b. This kind of component can be applied in micro devices at high

Shaping of the precursors:

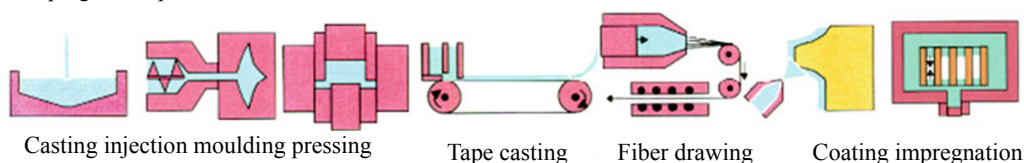


Fig. 24 Techniques applicable to the shaping of organic polymer precursors [20].

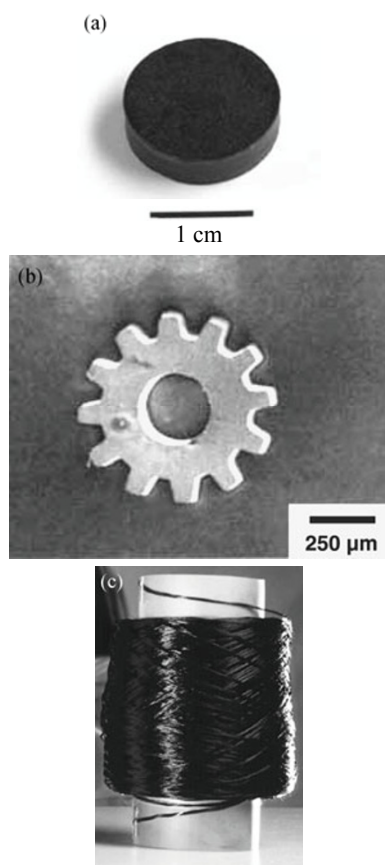


Fig. 25 The Si-B-C-N bulk ceramic (a) [12], micrometer gear (b) [17] and ceramic fiber (c) [65], prepared by the organic polymer pyrolyzing method.

temperatures, such as micro mechanical device, micro electronic circuit, micro turbine, and micro sensor etc. Additionally, pyrolyzing organic polymer can also produce a porous ceramic, which can be applied in the field of adsorption or filtration at high temperatures. Figure 25c displays the Si-B-C-N ceramic fiber prepared by the melt spinning method. The fiber generally has a smooth surface and a diameter of 8-14 μm . At 1500 $^{\circ}\text{C}$ or even higher temperatures in air, the Si-B-C-N fiber has a large tensile strength, high structural stability, and excellent oxidation resistance [65]. Therefore, the Si-B-C-N fibers have great practical values at high temperatures.

Research shows that adding reinforcing phases into polymer precursor may further increase the high-temperature mechanical properties of Si-B-C-N ceramics. Impregnating the melt polymer precursor into carbon-fiber woven fabrics and then pyrolyzing it at high temperatures will produce a $\text{C}_f/\text{Si-B-C-N}$ ceramic matrix composite, whose appearance is displayed in Fig. 26a [19]. Substituting the melt precursor with a kind of SiC-whisker-included polymer,

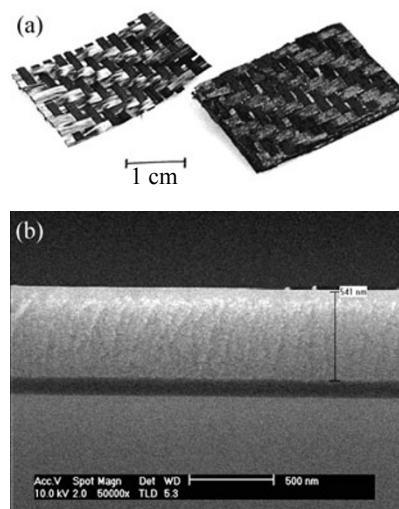


Fig. 26 Carbon fiber fabrics before (left) and after resin-transfer-molding and thermolysis (right) (a) [8], and the cross section morphology of the Si-B-C-N coating prepared by spinning and pyrolyzing technology on the surface of $\text{SiO}_2\text{-Si}$ (b) [74].

the product will be a $\text{C}_f/\text{SiC}_p/\text{Si-B-C-N}$ composite [73]. As compared with Si-B-C-N ceramic, these ceramic matrix composites generally have better structural stability, mechanical properties and creep resistance at high temperatures. They possess ductile fracture, no matter at room temperature, at elevated temperature, or even they are annealed at high temperatures for hours. Thus, they may be applied in high-performance brake sheet, or thermal protection materials on high-speed aircrafts. Employing dipping or painting method, one can also prepare Si-B-C-N coatings on carbon fibers or metals, as indicated in Fig. 26b. Since Si-B-C-N ceramic has nice structural stability and oxidation resistance, the coatings may be used as oxidation resistant or corrosion resistant materials.

5.2 Applications of the Si-B-C-N film prepared by reactive magnetron sputtering

At present, the Si-B-C-N film is mainly prepared by the reactive magnetron sputtering method. This method employs a simple operation, causes little pollution, and is able to produce ceramic films on various kinds of substrates. The as-deposited film has a smooth surface and a uniform thickness, as shown in Fig. 27. Research reveals that the film has a high structural stability, good oxidation resistance, high hardness, small thermal expansion coefficient, and small compressive stress on the interface [23]. Additionally, the film also

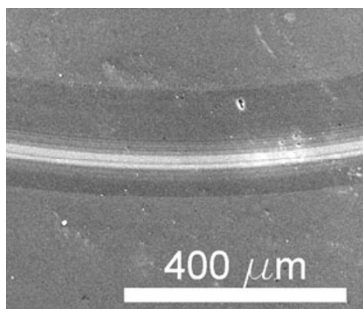


Fig. 27 SEM image of the alumina ball track on the Si-B-C-N film deposited by the reactive direct current magnetron co-sputtering on the surface of silicon [36].

has the characteristic of semiconductor, photoluminescence or light transmission [24]. The Si-B-C-N film may be applied in high-temperature photoelectron circuit, communication or control device.

5.3 Applications of the Si-B-C-N ceramic prepared by mechanical alloying plus sintering

The latest findings show that the Si-B-C-N bulk ceramic prepared by the mechanical alloying plus sintering method has a microstructure similar to that of some polymer-derived nano Si-B-C-N ceramics. However, the former has a simple preparation process, a higher relative density and a larger dimension, as displayed in Fig. 28. The diameter, thickness, relative density and room-temperature fracture strength of the ceramic sample is about 30 mm, 4.5 mm, 91%, and 331 MPa, respectively [37]. The image in Fig. 29 is the fracture morphology of the C_f /Si-B-C-N ceramic matrix composite, prepared by hot pressing the chopped-carbon-fibers-mixed Si-B-C-N powder at 1800 °C for 30 min. The composite manifests a ductile

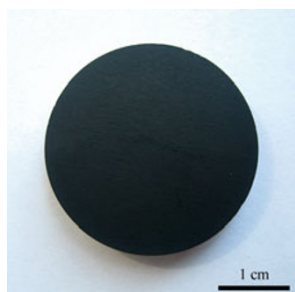


Fig. 28 Digital image of the bulk ceramic prepared from the mechanically alloyed Si-B-C-N powder [37].

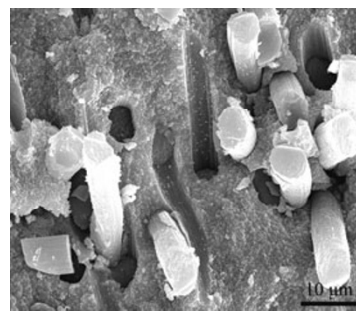


Fig. 29 Fractograph of the C_f /Si-B-C-N ceramic matrix composite prepared by hot pressing the Si-B-C-N powder mixed with chopped carbon fiber at 1800 °C for 30 min [75].

fracture mode, a nice resistance to thermal shock and to the erosion of high-temperature airflow. Thus, it is potentially used to fabricate structural or thermal protection components, serving at elevated temperature range.

6 Conclusions and outlook

Si-B-C-N ceramic attracts great attention in the past twenty years or so, because of its special structures and outstanding properties. Currently, the ceramic is mainly prepared by organic polymer pyrolyzing route, reactive magnetron sputtering and mechanical alloying plus sintering method. While most researchers focus on the polymer pyrolyzing route, the reactive magnetron sputtering and mechanical alloying plus sintering methods are only developed in recent years, thus the studies are still in their infancy. Much research work on the Si-B-C-N ceramic has been carried out in its raw materials, preparation process, microstructure, structural stability, oxidation resistance, creep resistance, fiber preparation, as well as film preparation and its relevant properties. The above mentioned three preparation methods have their own advantages, and the products may be widely applied, especially in the fields at high temperatures. However, disadvantages also exist in these methods, and theoretical research or application development of the Si-B-C-N ceramic is still confronted with many difficulties. In the future, further study is required on basic research, such as structural features, potential properties, oxidation mechanism or crystallization kinetics. At the same time, more efforts need to be made on the application research of this ceramic, including developing cheap or pollution-free raw

materials, increasing ceramic yield, exploring advanced operation process, optimizing processing parameters, and preparing dense bulk ceramics especially with large dimensions or ceramic products for various applications.

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